Supporting Information

Asymmetric Amination of 2-Substituted Indolin-3-ones Catalyzed by

Natural Cinchona Alkaloids

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1 General procedure for the synthesis of 2-substituted indolin-3-ones



(a) General synthetic method of 2-phenyl indolin-3-ones^[1]

To a solution of KOH (3.839 g, 68.4 mmol) and K_2CO_3 (4.149 g, 30.0 mmol) in H_2O (60 mL) was added glycine derivatives **5** (45 mmol, 1.5 equiv.) and **4** (30 mmol, 1 equiv.). Then Cu powder (10.8 mg) was added, and the mixture was refluxed for 12 h. After filtration, the filtrate was acidified with aqueous HCl (1 N, 120 mL), the formed precipitate was collected and dried over P_2O_5 in a desiccator under reduced pressure to give **6**.

To a solution of **6** (25 mmol, 1 equiv.) in Ac₂O (75 mL) was added NaOAc (37.5 mmol, 1.5 equiv.). The mixture was refluxed for 5 h, then cooled to 60 $^{\circ}$ C and concentrated under reduced pressure to remove Ac₂O. The residue was extracted with EtOAc (20 mL×4), the combined extract was washed with brine (20 mL) and dried over MgSO₄. After filtration, the filtrate was concentrated, the residue was dissolved in EtOH (60 mL), then a solution of Na₂SO₃ (37.5 mmol, 1.5 equiv.) in H₂O (20 mL) was added. The mixture was refluxed for 2 h, then the solvent was removed and H₂O (30 mL) was added. The mixture was extracted with EtOAc (40 mL×4), the combined extract was washed with brine (50 mL) and dried over MgSO₄. The organic solvent was evaporated, the residue was purified by flash column chromatography on silica gel to afford **1a**.

Substrates 1b-1j were synthesized according to the above procedure.



1a (5 mmol) and KOH (25 mmol) were added in EtOH (20 mL), the mixture was refluxed for 1 h, then cooled to rt and concentrated under reduced pressure to remove EtOH. The residue was extracted with EtOAc (10 mL×3), the combined extract was washed with brine (10 mL) and dried over Na₂SO₄. The organic solvent was evaporated, the residue was purified by flash column chromatography on silica gel to afford **1u**.

1u (3 mol) and NaOH (4.5 mmol) were dissolved in DMF (5 mL), and then benzyl bromide was slowly added. The solution was kept at room temperature for 15 h, then diluted with CH_2Cl_2 and purified by flash column chromatography on silica gel to afford 1v.

Compound 1v: 94% yield; white solid; ¹H NMR (400 MHz, Chloroform-d) δ 7.30 (m, 2H),

7.25–7.14 (m, 8H), 7.09 (m, 2H), 6.91 (t, J = 7.5 Hz, 1H), 6.65 (d, J = 7.8 Hz, 1H), 4.89 (d, J = 15.7 Hz, 1H), 4.67 (d, J = 15.7 Hz, 1H), 4.37 (s, 1H); ¹³C NMR (101 MHz, Chloroform-d) δ 177.8, 142.6, 140.4, 135.5, 132.1, 129.6, 128.9, 128.9, 128.6, 128.6, 128.2, 127.8, 127.3, 127.3, 125.5, 125.5, 125.0, 123.5, 109.7, 78.1, 44.0. ESI-HRMS: m/z [M+H]⁺ calcd. for C₂₆H₃₂N₃O₆: 300.1383, found: 300.1392

(b) General synthetic method of 2-benzyindolin-3-ones



1a (350 mg, 2 mmol, 1 equiv.) and DMF (5 mL) were added to a round-bottom flask. Then sodium hydride (1.2 equiv. in 5 mL DMF) was added slowly using a syringe at 0 °C. After the reaction mixture was stirred at 0 °C for 30 min, alkyl bromide (2.2 mmol, 1.1 equiv.) was slowly added. The solution was kept at room temperature for 20 h, then diluted with CH_2Cl_2 and purified by flash column chromatography on silica gel to afford **1n**.

Substrates **10-1t** were synthesized according to the above procedure.

2 References

[1] a) Rodr guez-Dom nguez, J. C.; Balbuzano-Deus, A.; López-López, M. A.; Kirsch, G. J. *Heterocyclic Chem.* 2007, 44, 273. b) Matsumoto, S.; Samata, D.; Akazome, M.; Ogura, K. *Tetrahedron Lett.* 2009, 50, 111.



3 Copies of ¹H and ¹³C NMR spectra of compounds 1s and 3a-3t





























































#	[[[[]]]]		[[[[]]]]	[IIIAU^S]	[mao]	6
1	4.628	MM R	0.0975	45.45885	7.76950	5.8631
2	5.766	MM R	0.2643	729.88220	46.01999	94.1369







6.398 MM R 0.3898 449.37311 19.21361 3.1490























峰	保留时间	类型	峰宽	峰面积	峰高	峰面积
#	[min]		[min]	[mAU*s]	[mAU]	00
1	4.722	MM R	0.2459	3235.48779	219.32024	50.3168
2	6.377	MM R	0.3943	3194.74707	135.04497	49.6832













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#	[min]		[min]	[mAU*s]	[mAU]	00	
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1	6.981	MM	0.5346	2.22634e4	694.03503	94.8631	
2	9.275	MM	0.5362	1205.56653	37.47159	5.1369	













